AD-A275 330

ENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1993	THESIS/DISSERTATION

4. TITLE AND SUBTITLE

Determination of Free Available Chlorine in Denitrified Wastewater Effluent

5. FUNDING NUMBERS

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

AFIT Student Attending: Univ of Florida

8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/CI/CIA-   93-152

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

DEPARTMENT OF THE AIR FORCE
AFIT/CI
2950 P STREET
WRIGHT-PATTERSON AFB OH 45433-7765

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release IAW 190-1
Distribution Unlimited
MICHAEL M. BRICKER, SMSgt, USAF
Chief Administration

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

DTIC
ELECTE
FEB 0 4 1994
A

94-03913

14. SUBJECT TERMS

15. NUMBER OF PAGES
45

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std 239-18
298-102

94 2 03 129

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DENITRIFIED WASTEWATER EFFLUENT

By:

RICHARD LLOYD MATTA

A REPORT PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING
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Abstract

The DPD and amperometric methods for determining free available chlorine were compared in a study of chlorine demand in a denitrified (unchlorinated) wastewater. The DPD method was found to be more precise than the amperometric method. Chlorine demand of denitrified wastewater from the Kanapaha Water Reclamation Facility (KWRF) was found to increase with increase in chlorine dose. Total chlorine demand was found to increase with time when dose was constant. These results support previous work at the KWRF which found increased chlorine demand with chlorine dose. Synthetic (laboratory prepared) water was spiked with ammonium chloride at various concentrations to determine the effect of chloramines on the free chlorine measurement. The interference of chloramines, particularly monochloramine, on the free available chlorine residual measurements made using the DPD method was significant. The amperometric method showed no such interference.

Introduction

History of Chlorine Usage

The use of chlorine dates back nearly one hundred and forty years, when, in 1854, London sewage was deodorized with chlorine. The notion then was that disease was spread by odors, not germs. In 1880, studies proved pathogenic bacteria caused specific diseases[1]. In the United States, the first use of chlorine as a disinfectant occurred in 1893, in Brewster, New York. For nearly the first half of the twentieth century, interest in chlorine centered around its ability in wastewater treatment to prevent septicity, control hydrogen sulfide generation in collection systems and treatment plants, and control odor[1]. In the final analysis, this versatile oxidizing agent's use will be driven by the need for treatment plant operators to comply with local, state, and federal regulatory demands designed to protect the public health and the environment. In fact, the 1972 Federal Water Pollution Control Act requires that all wastewater treatment plants in the United States disinfect wastewater prior to discharge to the environment[2]. Since the Kanapaha Water Reclamation Facility (KWRF) discharges wastewater effluent into the Floridan Aquifer, a drinking water aquifer, discharges must comply with strict standards which are strongly related to the natural composition of receiving waters. Among the standards are limitations on fecal coliform bacteria concentration, as well as the concentration of trihalomethanes (THMs), a disinfection by-product, in the discharged effluent.

Kanapaha Waste Water Treatment Plant

In this study, the wastewater treatment plant effluent of concern is that of the

Kanapaha Water Reclamation Facility (KWRF). This treatment plant is designed to handle 10 million gallons per day of influent domestic sewage from the City of Gainesville. After a modified Ludzak-Ettinger treatment regime entailing biological nitrification, then denitrification, wastewater is filtered, chlorinated at 6-12 mg chlorine (Cl_2/l) with a contact time of two hours, then routed through discharge wells to the Floridan aquifer[3]. To ensure that a chlorine dose is adequate to maintain a sufficient free available chlorine (FAC) residual after the contact time, the residual must be routinely checked. This enables the plant operator to adjust the chlorine dose to the demand, which varies throughout the day.

The performance of the DPD and amperometric tests for determining free chlorine in wastewater is one consideration of this paper. The relationship of chlorine dose to demand will also be studied in this paper. Research by Kotob[3] at the KWRF on trihalomethane formation potential during chlorination of wastewater identified increased chlorine demand as a function of chlorine dose. Before proceeding, however, it is worthwhile to discuss which FAC methods were selected for FAC tests done in this research.

Testing for Chlorine Residual

The search for the most precise, accurate, and sensitive tests to determine chlorine residual began at the turn of the century. In 1913, the only method used for measuring chlorine residual was the iodometric (starch-iodide) method. This method is very useful for determining high concentrations of chlorine (1 mg/l or greater), but was too limited by this lack of sensitivity to meet testing needs[4]. That different chlorine

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residuals exist as free available chlorine (hypochorous acid, hypochlorite ion, and aqueous chlorine, $Cl_{2(aq)}$) and combined chlorine (monochloramine, dichloramine, and nitrogen trichloride) was not realized until 1939 when the breakthrough phenomena was demonstrated and empirically studied[1]. At this point, sensitivity of testing for FAC became paramount. This was motivated by differences in bactericidal properties of FAC versus combined chlorine[5]. Hypochlorous acid is a potent disinfectant. As a neutral molecule resembling water in structure, it diffuses across cell membranes quite easily. Chloramines, such as monochloramine, are much weaker oxidizing agents because chlorine is less electropositive in these molecules (due to oxygen's greater electronegativity than nitrogen). Chloramines diffuse slowly through the bacteral cell wall because they are dissimilar to water in structure. The relative germicidal activity of monochloramine to hypochlorous acid was reported to be 1/36th[6].

Testing for Free Available Chlorine

For nearly forty years after the characterization of chlorine residual, research continued in the development, comparison, and modifications of methods to measure FAC. W.J. Cooper, one of a small group of chemists at the forefront of published studies between 1973 and 1983 stated, "the aim was to find an acceptable procedure which must also be rapid, convenient, accurate, and precise over the wide ranging character of wastewaters encountered[7]." Most of these testing procedures fell into one of three categories: iodometric titration, colorimetric methods, and electrode methods. As discussed already, the iodometric method is limited by its poor sensitivity and lack of specificity for FAC over other oxidizing agents. The major colorimetric methods include

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the DPD test, leuco crystal violet (LCV) test, free available chlorine test by syringaldazine (FACTS), and the stabilized neutral orthotolidine test (SNORT)[4,6]. The electrode method most studied is the amperometric method.

Three methods were selected for use in this research. These were the DPD method, FACTS method, and amperometric method. One major reason these traditional methods were chosen and the subject of several equivalency testing procedure articles in the literature, is their proven accuracy and precision. Interferences from combined chlorine is a common problem in FAC testing procedures[7]. The amperometric and FACTS methods were found most insensitive to this interference. The DPD test was exceptionally precise and accurate when combined chlorine was absent[6]. A modification to the DPD colorimetric test called DPD-Steadifac was studied by Cooper. This method requires addition of thioacetamide to the test solution (after the DPD indicator is added). Cooper found thioacetamide prevented intrusion into the FAC readings from monochloramine and dichloramine[9]. The DPD-Steadifac procedure was not used in this experiment. Thus, the effects of chloramines on FAC readings obtained from the traditional and routinely used DPD testing procedure could be experimentally studied.

Objectives

The major objectives of this study were:

1. to compare the accuracy and precision of the DPD, amperometric, and FACTS methods for measuring free chlorine in Kanapaha wastewater samples

2. to evaluate and explain the chlorine demand versus chlorine dose

relationship based on results obtained with methods chosen

3. to study the interference of combined chlorine on FAC residuals measured by the methods used in this report

METHODS AND MATERIALS

A description of each of the methods used in this research follows.

Amperometric Titration

Figure 1 shows the Fisher CL Titrimeter Model 397 used in this research. The amperometric titrator measures current in microammeters with a platinum electrode (through which voltage is applied) placed in the sample. The microammeter reading indicates the concentration of all chemical species in solution which can be reduced at the applied voltage. A 0.05 molar phosphate buffer, prepared to ensure it is chlorine-demand free is used to maintain a pH between 6.5 and 7.5[10]. Three milliliters of the buffer is used for each titration. A manually controlled peristalic pump is used to deliver a 0.00564N phenylarsine oxide solution (Fisher No So-P-68) to the sample through a pipet. The sample volume selected is chosen so that no more than 2 ml of titrant is required. The phenyarsine oxide reduces the free chlorine in the sample according to the following reaction

$$C_6H_5AsO + HOCl + H_2O \rightarrow C_6H_5AsO(OH)_2 + HCl \qquad (1)$$
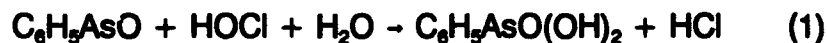
As this reaction proceeds, the microammeter reading decreases indicating a loss of chlorine. The meter acts as a null-point indicator, i.e., the actual meter reading is not

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Fisher
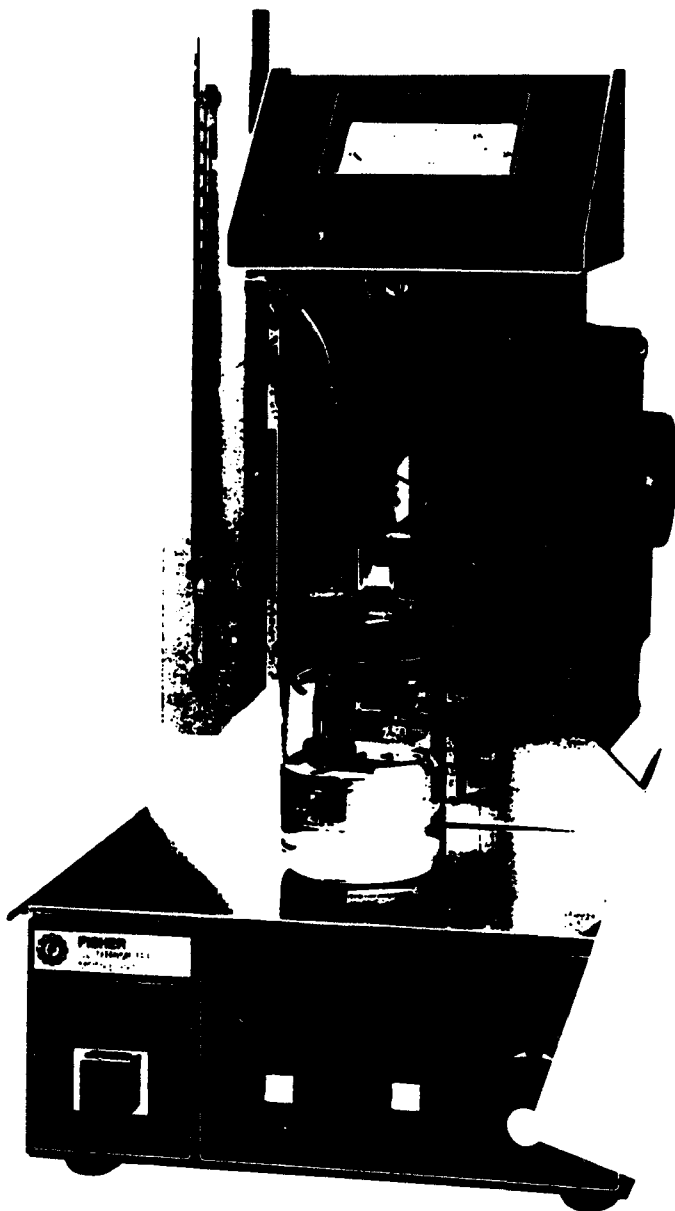# CL Titrimeter
Model 397

Figure 1 Amperometric Titrator

as important as the relative readings as the titration progresses. The endpoint is achieved when an additional volume of titrating solution added does not cause the ammeter reading to drop. The volume of titrant in ml consumed just prior to addition of titrant causing no additional decrease in the microammeter reading is equivalent to the free available chlorine concentration (mg Cl_2/l)[11]. A more detailed narrative of this procedure is contained in Appendix 1. This narrative should be very useful to the novice using amperometric titration since this method requires more operator skill and experience than other methods commonly used to measure chlorine residual.

DPD Method

The DPD method, a colorimetric test, was used with a Perkin-Elmer Model 552 spectrophotometer, set to an absorption maxima of 515 nm, to measure chlorine residual. A DPD packet from Hach Co. was added to the 25 ml container with sample and the test tube was inverted three times. The DPD packet contains reagent (indicator) and buffer. Afterward, a cuvette (cuvette path length 1cm) was filled with the sample and analyzed with the spectrophotometer one minute after initially adding the DPD packet to the sample. To minimize potential interference caused by undissolved powder getting into the cuvette, a small amount of the 25 ml sample was poured out (with some of the looser indicator particles) prior to careful addition of sample to the cuvette. In order to relate absorbance values obtained for samples and FAC concentration, a calibration curve was developed.

The spectrophotometer was calibrated and a standard curve developed by preparing chlorine standards in the range of 0.05 to 3 mg/l chlorine[10]. At 4 mg Cl_2/l, non-

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linearity was observed in the standard curve although Standard Methods implies the curve should be linear to 4 mg/l. Data generated and used to make the curve and regression analysis are in Table 1. The standard curve is shown in Figure 2. The coefficient of determination (R^2) for this curve was 0.999 showing excellent linearity between absorbance and concentration. The equation for calculating regressed absorbance values is

$$Abs = 0.266*Conc + 0.001 \quad \text{(eqn 2)}$$

where Conc = free available chlorine concentration in mg/l. The regression line deviated very slightly from the origin when plotted. Cooper, et al. noted this slight deviation from Beer's law as a consistent characteristic of the DPD method[9]. In their study, they found an intercept value of 0.016, slightly higher than that found in this research. A positive intercept value indicates that at a zero chlorine concentration, there will be absorbance.

Beer's law states that when an incident beam of radiation strikes a surface which is perpendicular to the beam's travel direction, there will be a change in the incident power of the beam and the ratio of this change to the original beam power will be directly proportional to the ratio of the change in the capture area of absorbing species to the total surface area. In its integrated form which is presented in equation 3, Beer's law states that absorbance is the product of concentration and a coefficient comprising the path length and molar absorptivity[12].

$$Abs = e*b*Conc \quad \text{(eqn 3)}$$

Using a 1 mg/l chlorine concentration, and a known path length (b) of 1 cm, the

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TABLE 1

DATA FOR CALIBRATION CURVE

CONCENTRATION (MG/L)	ABSORBANCE Sample 1	Sample 2	AVERAGE	REGRESSED ABSORPTION
0.00	0.000	0.000	0.000	0.001
0.05	0.012	0.010	0.011	0.014
0.20	0.050	0.049	0.050	0.054
0.50	0.132	0.134	0.133	0.134
0.80	0.220	0.220	0.220	0.214
1.00	0.274	0.276	0.275	0.267
2.00	0.533	0.536	0.535	0.534
3.00	0.793	0.799	0.796	0.800

Regression Output:

Constant	0.00100
Std Err of Y Est	0.00495
R Squared	0.99974
No. of Observations	8.00000
Degrees of Freedom	6.00000
X Coefficient(s)	0.26636
Std Err of Coef.	0.00177

CHLORINE CALIBRATION CURVE
7/23/93
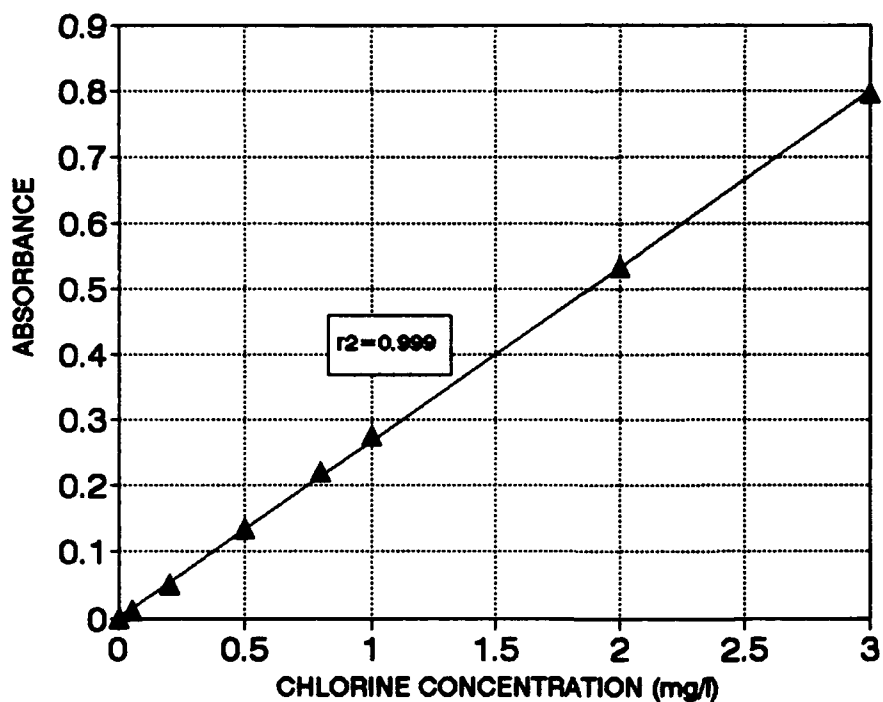
Figure 2

molar absorptivity (e) of this method can be determined. From eqns 2 and 3, the molar absorptivity is $1.89*10^4 Lmol^{-1}cm^{-1}$. Cooper, et al. found a value of $1.5*10^4 Lmol^{-1}cm^{-1}$ for the molar absorptivity for standard chlorine solutions prepared in DDI[9]. The molar absorptivity is important because it shows the sensitivity of the absorbance to the concentration.

Additional quality assurance procedures used for this method include careful cleaning of the outside of each cuvette prior to insertion into the spectrophotometer and transfer of samples as well as handling of cuvettes so as to practically eliminate interference from air bubbles in the cuvettes.

Facts Method

The FACTS colorimetric method was attempted by this researcher but the method was eliminated from further consideration after several difficulties were encountered over a period of a month. The method involved making an indicator which is a saturated solution of syringaldazine by adding 115 mg of syringaldazine (3,5-dimethoxy-4-hydroxybenzaldazine) obtained from Aldrich Chemical Co. to 2-propanol (Fisher Scientific)[10,13]. This reagent reacts on a 1:1 molar basis with chlorine to yield a colored product which can then be analyzed with a spectrophotometer at 530 nm. Samples were buffered with a 0.5 molar phosphate buffer (pH 6.7) to maintain a pH of the sample/buffer/syringaldazine mixture at 6.5 to 6.8.

The procedure called for adding to 3 ml of sample with FAC residual of 0.1-10 mg/l, 0.1 ml buffer, then 1 ml syringaldazine reagent to a tube, then inverting twice prior to reading absorbance[10]. As suggested in the literature, samples were analyzed within

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30 seconds to a minute. Within this time frame, Cooper, et al. found color development complete and fading minimal[5,13]. A standard curve needed to be prepared by using chlorine doses covering the 0.1 mg/l to 10 mg/l range and following the procedure outlined above. The problems encountered in exploring this method are summarized in Appendix 2. They include great difficulty in dissolving the syringaldazine, chlorine demand of the 2-propanol, and the inability to dissolve sufficient indicator in DDI for a successful reaction. Since reasonable precision could not be obtained with this method, it was abandoned.

Sample Collection and Treatment

Samples consisted of either synthetic (laboratory) samples or samples collected from the KWRF. Laboratory samples were prepared with double-deionized water which was shown in this research to be chlorine-demand-free. To demonstrate this, DDI water was dosed at the beginning of the experimental period with chlorine and its absorbance was measured by the DPD method. The vessel containing the DDI water and chlorine was then covered and placed in the dark. Twenty-four hours later the absorbance was checked again. On several such runs, no change in absorbance was noted. During the actual experimentation period, DDI/chlorine controls were periodically run using the method described above over the reaction time and these, too, showed the DDI water to be chlorine-demand-free.

Two gallon grab samples of unchlorinated effluent were collected from an open basin which receives the filter effluent at the KWRF. These samples were transported in an ice-filled cooler, then kept in the dark and covered until portions were removed for

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experiments. Samples were used the same day they were collected.

Samples were dosed using stock sodium hypochlorite solutions made from an original grade sodium hypochorite solution (Fisher) of 4-6% chlorine (as Cl_2). Volumes of stock were diluted with chlorine-demand-free DDI water to make working stock solutions. Stock chlorine solutions were standardized daily using the traditional starch-iodide endpoint in the Iodometric B method[10]. A fresh 0.0098N sodium thiosulfate solution was used and it was standardized against 0.01N potassium bi-iodate. A 400 mg/l working stock chlorine solution was used for the experiments in order to minimize the chlorine dose volume/sample volume (a potential dilution effect as the volume of chlorine solution added increases for solutions at higher doses).

Chlorine dosed samples (and blanks) were placed in a closed cabinet to exclude light. Reaction vessels used were chosen to keep head-space to a minimum. This method for minimizing chlorine loss to anything other than chlorine demand in the sample is supported by tests conducted by Cooper, et al. They found that when a chlorine-dosed sample was left in an open beaker and exposed to light in their their laboratory, up to 20 % loss in FAC occurred in the first hour. When the beakers were placed under cardboard, no FAC loss was measured. The researchers determined the major pathway for loss was photolysis rather than gaseous diffusion by placing a cardboard box which allowed for some air flow over the beakers, then measuring FAC after an hour. No FAC loss was measured[8].

Glassware

Glassware used was cleaned with soap, then triple rinsed with tap water, deionized

water, then double-deionized water. Glassware was then soaked in 10mg/l chlorine solution for a minimum of 3 hours to remove any chlorine demand. Afterward it was vigorously rinsed five times with double-deionized water to remove any residual chlorine. Periodic testing of a volume of water transferred between six just rinsed pieces of glassware using the DPD method conclusively proved the efficacy of this method of removing chlorine from glassware.

Quality Assurance

The method detection limit and percent recoveries were determined for both methods. A sample (DDI) was dosed at 1 mg/l chlorine, and buffered to about pH 7 with 0.05 molar phosphate buffer, then analyzed 24 hours later for free available chlorine residual. Seven runs were made with both analytical techniques.

Both the amperometric and DPD analyses were performed. Using section 1030 E "Method Detection Limit" in the 1992 Standard Methods, MDL's were calculated. Results are shown in Table 2. The MDL's were 0.06 mg/l for the DPD method and 0.08 mg/l for the amperometric method. These MDL's were determined based on DDI dosed with chlorine, not wastewater effluent or synthetic laboratory samples; therefore, variance introduced by the KWRF sample matrix is not accounted for. The MDLs for the KWRF would likely be greater. The MDL provides a 99% assurance that at this level of measurement, the value obtained is chlorine being detected and not error due to the analytical methodology used. Gordon, et al. reported detection limits of 0.02-0.03 and 0.01 mg chlorine/l for the amperometric titrator and the DPD methods, respectively. They did not, however, provide a confidence interval around their detection limits[4].

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TABLE 2

METHOD DETECTION LIMIT		
1.0 mg/l CHLORINE DOSE IN DDI		
24 HOUR REACTION TIME		
	RESIDUAL CHLORINE (mg Cl2/l)	
RUN #	DPD	AMPEROMETRIC
1	0.94	0.91
2	1.00	0.92
3	1.00	0.95
4	0.99	0.93
5	1.00	0.91
6	0.99	0.97
7	0.99	0.97
MEAN	0.99	0.94
STD DEV	0.020	0.026
MDL	0.06	0.08
NOTE: MDL=3.14*(STD DEV)		

Percent recoveries expressed as mean 100*FAC/dose were 99.0 for the DPD method and 94.0 for the amperometric method after the 24 hour contact period with a 1 mg/l chlorine dose in DDI. Chlorine evaporation during amperometric titration is known to be a problem, as this may explain the recovery differential. Nicolson found that with a commercial titrator, at a chlorine dose of 0.1 ppm, 85.7% was recovered; at a dose of 0.5 ppm, 86.5% was recovered over the titration time[14]. Nicolson's titration lasted under two minutes.

Description of Experimental Methods

The first experiment involved dosing filtered effluent samples (prior to chlorination) collected at the KWRF with 8 mg/l chlorine. Samples were collected on three different days and 4 analyses were run each day with both the DPD and amperometric methods

after a 2 hour reaction time. Amperometric samples were dosed at half-hour intervals to ensure a two hour reaction time in each sample. Results were compared to determine the accuracy and precision of each method, and to determine which method performed better. Results are presented in "Results and Discussion" later in this paper.

The second experiment involved examination of chlorine demand versus dose. Filtered effluent wastewater from the Kanapaha treatment plant was collected and dosed with chlorine. After a two hour reaction time, the chlorine residual was measured with both the amperometric and DPD methods in aliquots which had been dosed at either 8, 12, or 16 mg/l chlorine. Sample dosing was staggered to ensure a two hour reaction time upon analysis. At each dose, 4 separate aliquots of the original sample were analyzed.

The third experiment involved determining the effect of ammonium chloride on measurements provided by both techniques. An ammonium chloride standard was prepared at a concentration of 100 mg/l as nitrogen. A dose of 1 mg/l ammonium chloride as N was made to buffered DDI samples. Staggered chlorine dosing at chlorine-to-nitrogen mass ratios of 4, 6, and 12 were made. Then three analyses were made at each concentration after a two hour reaction time for FAC residual.

RESULTS AND DISCUSSION

Accuracy and Precision of the Methods

On three separate days, Kanapaha wastewater samples were collected, dosed

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at 8 mg/l chlorine, and allowed to react for two hours. At the end of this time, four aliquots were analyzed by the DPD method and another four analyzed by the amperometric method for free available chlorine. Results are tabulated in Table 3. One consistent trend noted in the results is the lower FAC measured by the amperometric method than the DPD method. Percent differences between the mean FAC for DPD versus amperometric method (using the latter as the reference value) for days one through three were 1.27, 1.49, and 12.33, respectively. Also notable is the high degree of precision among the DPD results. The mean range over the three days was just 0.05 mg Cl_2/l. The mean standard deviation was only 0.03. Precision was not as good for the amperometric titration results in this experiment. The mean range was 0.25 mg Cl_2/l, while the mean standard deviation was 0.15 mg/l. These accuracy and precision values agree well with what was found in the literature. Gordon, et al., in their comprehensive literature review, reported expected accuracy of +/- 1-15% and expected precision of +/- 1-14% for the DPD colorimetric method. For the amperometric method, they reported 3-50% expected precision[4]. No information was provided on expected accuracy for amperometric titration, probably because the amperometric titrator is usually used as the reference for other procedures.

Statistical comparisons were made between mean daily FAC values and also between the mean FAC values obtained from each method for each of the three days. Using a one-tailed t-test at a 95% confidence level, the mean FAC values obtained by the DPD were not significantly different for days 2 and 3. For the amperometric method, FAC residuals measured on days 1 and 3 were not significantly different at this confidence

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TABLE 3

COMPARISON OF ACCURACY AND PRECISION OF DPD METHOD VS AMPEROMETRIC METHOD FOR MEASURING CHLORINE RESIDUAL KANAPAHA WASTEWATER 2 HOUR CONTACT TIME WITH DOSE OF 8 mg/l CHLORINE			
DPD METHOD **DILUTION 4:1**		**AMPEROMETRIC METHOD** **DILUTION 4:1**	
ABSORBANCE	CONCENTRATION (mg Cl2/l)	VOL (ml) TITRANT	CONCENTRATION
DAY 1 0.214	3.20	0.81	3.24
0.214	3.20	0.74	2.96
0.214	3.20	0.78	3.12
0.211	3.15	0.82	3.28
RANGE	0.05	RANGE	0.16
MEAN	3.19	MEAN	3.15
STD DEV	0.023	STD DEV	0.144
DAY 2 0.227	3.39	0.81	3.24
0.227	3.39	0.85	3.40
0.228	3.41	0.81	3.24
0.227	3.39	0.88	3.52
RANGE	0.02	RANGE	0.28
MEAN	3.40	MEAN	3.35
STD DEV	0.008	STD DEV	0.136
DAY 3 0.228	3.47	0.79	3.16
0.222	3.37	0.72	2.88
0.219	3.32	0.78	3.12
0.219	3.32	0.71	2.84
RANGE	0.14	RANGE	0.32
MEAN	3.37	MEAN	3.00
STD DEV	0.068	STD DEV	0.163
MEAN RANGE	0.05	MEAN RANGE	0.25
MEAN STD DEV	0.033	MEAN STD DEV	0.148
PERCENT DIFFERENCE DAILY MEAN FAC FOR DPD VS AMPEROMETRIC (DPD FAC-AMP FAC)/AMP FAC			
DAY 1 1.27	DAY 2 1.49	DAY 3	12.33

level. Samples analyzed in this research were collected at about the same time each day. Chlorine demand varies throughout the day and from day-to-day; hence, the similarity between results is only an observation and not a general statement regarding chlorine demands at other times, or even other days.

When the mean FAC residuals measured by both methods for each day were compared, greater significance in the hypothesis that the means were equal was obtained. For days 1 and 2, the calculated t-values were 1.55 and 0.73, respectively. Therefore, there is a high degree of confidence that there was no significant difference in the means since the t-value for 95% confidence is 1.94. On day 3, however, there was a significant difference (at this confidence level) in the mean FAC values obtained. This is reflected in the difference of 0.37 mg/l in residual FAC measured by the two techniques.

The percent difference between the DPD FAC measurement versus the amperometric method results is supported by Nicolson's work which was discussed previously. The twelve percent difference in measured FAC on day 3 was most likely the result of several compounding factors which probably contributed to error in the amperometric measurements.

Some possible reasons follow. Whereas the DPD samples were collected from the same reaction vessel in which sample had been chlorinated, then left to react, the samples for the amperometric method were individually dosed with chlorine, then left to react. This potentially introduced error in chlorine dosing. Additionally, all four of the DPD samples were analyzed within five to 10 minutes with very little agitation of the

chlorinated sample. With the amperometric method, each sample run took about 15 minutes during which the chorinated sample was rapidly stirred. The time to run each sample varied somewhat depending on how much needle fluctuation there was before final readings could be taken. Finally, while operator error is minimized because of the simplicity of the DPD method, the amperometric method is more involved and errors such as unnoticed bubbles in the titrating agent delivery system, inadequate DDI rinsing of the equipment, and an unclean electrode can all affect analyses. As Gordon, et al. pointed out, "volatility of the disinfectants makes sampling and sample handling major contributors to inaccuracy and imprecision[4].

There is some inconsistency in the literature about how quickly the titrating agent in the amperometric procedure should be added to the sample. There are two concerns: too lengthy a titration can lead to unacceptably high chlorine losses through volatility; too little reaction time may suggest an endpoint which really has not been achieved, and contribute to errors due to under-titration. Nicolson, who completed titrations in under two minutes for 0.5 mg/l chlorine residuals, even had doubts as to whether the reaction between chlorine and phenylarsine oxide proceeded to completion in "a reasonably short time." He found a slightly positive reaction when he used a colorimetric method (for measurement of chlorine) to analyze the solution he believed was just amperometrically titrated to the endpoint[14].

Guter, et al. used the amperometric titrator as a reference to which other FAC measuring methods would be compared. After dosing samples, they amperometrically analyzed the samples by adding 90% of the titrating solution to the sample before

turning on the cell stirrer, and then they completed the titration as quickly as possible[7].

According to Fisher Scientific technical representatives in the electrode department, a reasonable titration time is 10 minutes. They recommended adding titrating agent at 0.2 ml intervals until the endpoint is approached, then decreasing the volume added to the endpoint. After each addition of titrant, the meter should be stable before proceeding.

Standard Methods directs the amperometric operator to add titrant in progressively smaller increments until all meter movement ceases. Then to subtract the last increment to cause no meter response[10].

To achieve accurate results while minimizing the potential for error is one of the reasons the amperometric technique requires a skilled operator. As discussed in Appendix 1, a major factor affecting speed of titration is the initial concentration of FAC present in the sample. More than 1 mg/l of chlorine on the low sensitivity scale may require more time for the meter to stabilize, while on the high sensitivity scale, this researcher found that for the titrator used in this experiment, more that 0.3 mg/l caused significant time for the meter to stabilize. Practice with known solution concentrations is the best way to find the most suitable operator technique for a particular titrator.

Effect of Chlorine Dose on Measured Chlorine Demand

In experiment two, chlorine demand of Kanapaha wastewater after a two hour contact time with varying concentrations of chlorine dose was determined. FAC was measured with both the DPD method and the amperometric method. After twenty four

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hours the DPD method was used to check chlorine residuals again.

The very question of why there is continued chlorine demand after the breakpoint deserves attention. The KWRF wastewater effluent may contain from 1-3 mg/l organic nitrogen[1]. Organic nitrogen comes in many forms such as organic amines and amides. Their source is amino acids and various nitrogenous compounds of urine[1]. Chlorine reacts with these compounds in an electrophilic role, and reaction rates are related to reactant concentrations and the base strength of the amines or amide. Some amines react extremely quickly as a consequence of their basicity, even faster than monochloramine[15]. Many of the organic nitrogen compounds take days to react for kinetic reasons.

Reaction rates among the organic nitrogens vary greatly, largely as a consequence of reactant concentrations and the differing electrochemical properties of the organic nitrogens. When a reactant is present in only minute concentrations, the reaction rate may be extremely small due to rare collisions between reacting molecules. The chemistry of amines and amides is largely related to the nonbonded electrons on the nitrogen atom. Amides react very slowly because these electrons are delocalized from the nitrogen, thus reducing their basicity. The resonance interaction between nitrogen and the carbonyl group enhances intermolecular attraction, thus making the molecule less likely to react with chlorine when the molecules interact. Amines are generally much more reactive than amides because the non-bonded electrons are often available to engage in bonding. The methylamines, for example, have pk_b values comparable to that for ammonia: 4.75 for ammonia; 3.37 for methylamine; 3.22 for dimethylamine; 4.20 for

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trimethylamine.   Pyrrole, however, has a pk_b value of 13.60 which reflects the delocalization of nonbonded nitrogen electrons to the π systems in the molecule. Amides have pk_b values which are even greater than that for pyrrole.[16]

Another major source of chlorine demand in these ammonia-free waters is organic material. Humic substances are said to constitute 50% of the soluble organic matter in sewage effluents[2]. Humic substances can account for chlorine demands which vary with the type of humic materials present and their concentration.   Other factors affecting chlorine demand in chlorine-humic material interaction are pH, temperature, chlorine dose, and reaction time.   Chlorine is known, for example, to react readily with phenols, a common functional group of humic materials. The number of phenol functional groups varies with each humic molecule and can range from 9-38% of the total number of functional groups on the molecule[15].

Besides humic materials, wastewater effluents contain aromatic and heterocyclic organic compounds which chlorine can react with. Oxidation may be the predominant reaction, while substitution and addition also occur. Fifty chloro-organic constituents were separated by high pressure liquid chromatography from another secondary sewage effluent which had been sampled, dosed, and allowed to react for the contact time of the source treatment plant. In another study it was found that after chlorination of secondary sewage effluent, yields of chloro-organics as chlorine accounted for about 1% of the original chlorine dosage. This did not account for chlorine which may have reacted to form trihalomethanes or chlorinated humic materials[17]. It would not be anticipated that humic materials would exert a significantly different chlorine demand.

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Trihalomethanes are a reaction product of organic material and free available chlorine residual. Their source is largely humic substances. Stevens, et al. conducted experiments in which they found excellent correlation between THM formation caused by reaction of FAC with treated water and its formation in solutions prepared with commercially available humic acids at similar concentrations to those in the treated river water. They also found that low molecular weight substances containing the acetyl group were precursors for trihalomethane formation[18].

Kotob[3] measured THMs in KWRF wastewater. Using his findings, chlorine demand by the THMs can be estimated. At the highest chlorine dose he applied and after a 24 hour reaction time, he measured 132 ug/l THM. The THM which contains the most chlorine is chloroform. If it were assumed all the THM were chloroform, the chlorine demand of THM (as substituted chlorine) would be 0.12 mg/l. This example is very simplistic because it does not account for the many mechanisms involved in THM formation, some of which involve reduction of chlorine as it oxidizes humic materials.

The results obtained in experiment 2 (measurement of chlorine demand at several doses) are presented in Table 4. Much higher ranges and standard deviations are seen for the amperometric titrations than the DPD method. This is not surprising since the literature supports DPD as the most precise procedure for measuring FAC[8,13]. Another major factor which explains these findings is that in this experiment, one chlorinated sample was used for all the DPD runs, while many individually chlorinated samples were used for amperometric titration.

Chlorine demand as a function of dose is plotted in Figure 3 for both these

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methods. Chlorine demand as a function of dose increased as measured by the DPD method and the amperometric method. In fact, the DPD results show that for the same reaction time, the chlorine demand increased 1.08 mg/l when the dose was increased from 8 to 16 mg/l. Amperometric results show chlorine demand increasing with dose up to 12 mg/l, then levelling off as dose was increased further. At the 12 mg/l dose, the third result obtained with the amperometric method appeared to be an outlier. The measured residual of 5.68 mg/l was compared to the other results for this chlorine dose and determined to be more than 5 standard deviations from the mean of the three other analyses. Therefore, this value was not used in subsequent calculations (mean and standard deviation) nor in the preparation of Figure 3.

Two years ago, Mazen Kotob, a University of Florida graduate student, studied trihalomethane formation during chlorination of wastewater. As part of his study, he measured chlorine residuals with the same DPD method used in this research at various chlorine doses and contact times. Results obtained in this study are compared to his chlorine demand results as a function of dose. Table 5 presents chlorine demand found in Kotob's work and this research. These results are depicted in Figure 4. Data collected in this study to make the 24 hour comparison with his results are in Table 6. The slopes of the lines between the points in Figure 6 support the theory that to a point, as chlorine dose applied is increased, the change in demand increases rapidly, then decreases. For the 2 hour contact time, slopes for lines connecting the 8 mg/l point to the 12 mg/l point were 0.24 and 0.15 for 91' and 93' results, respectively. Between the 12 mg/l dose and the 16 mg/l dose points, the slopes were -0.05 and 0.12 for 91' and 93' results,

THE INFLUENCE OF CHLORINE DOSE ON DEMAND OF KANAPAHA WASTEWATER AFTER A 2 HOUR CONTACT TIME WITH RESIDUAL CHLORINE MEASURED BY THE DPD AND AMPEROMETRIC METHODS

DOSE CL2	ABSORBANCE	RESID CONC	DEMAND	VOL.TITRANT	CONC RESID	CHL DEMAND
	DPD METHOD			**AMPEROMETRIC METHOD**		
				DILUTION 4:1		
8 MG/L	0.220	3.29	4.71	0.83	3.32	4.68
DILUTION 4:1	0.215	3.21	4.79	0.84	3.36	4.64
	0.220	3.29	4.71	0.80	3.20	4.80
	0.217	3.24	4.76	See note 1		
	MEAN	3.26	4.74	MEAN	3.29	4.71
	STD DEV	0.037	0.037	STD DEV	0.083	0.083
				DILUTION 4:1		
12MG/L	0.440	8.59	5.41	1.60	6.40	5.60
	0.449	8.73	5.27	1.58	6.32	5.68
DILUTION 4:1	0.444	8.65	5.35	1.42	5.68 (Note 2)	12.00
	0.443	8.64	5.36	1.65	6.60	5.40
	MEAN	8.65	5.35	MEAN	6.44	5.56
	STD DEV	0.058	0.058	STD DEV	0.144	0.144
				DILUTION 8:1		
16 MG/L	0.546	10.23	5.77	1.33	10.64	5.36
DILUTION 5:1	0.540	10.12	5.88	1.28	10.24	5.76
	0.547	10.25	5.75	1.28	10.24	5.76
	0.540	10.12	5.88	1.33	10.64	5.36
	MEAN	10.18	5.82	MEAN	10.44	5.56
	STD DEV	0.071	0.071	STD DEV	0.231	0.231

Notes: Note 1: Sample Spilled
Note 2: Outlier Value

CHLORINE DEMAND VS CL2 DOSE
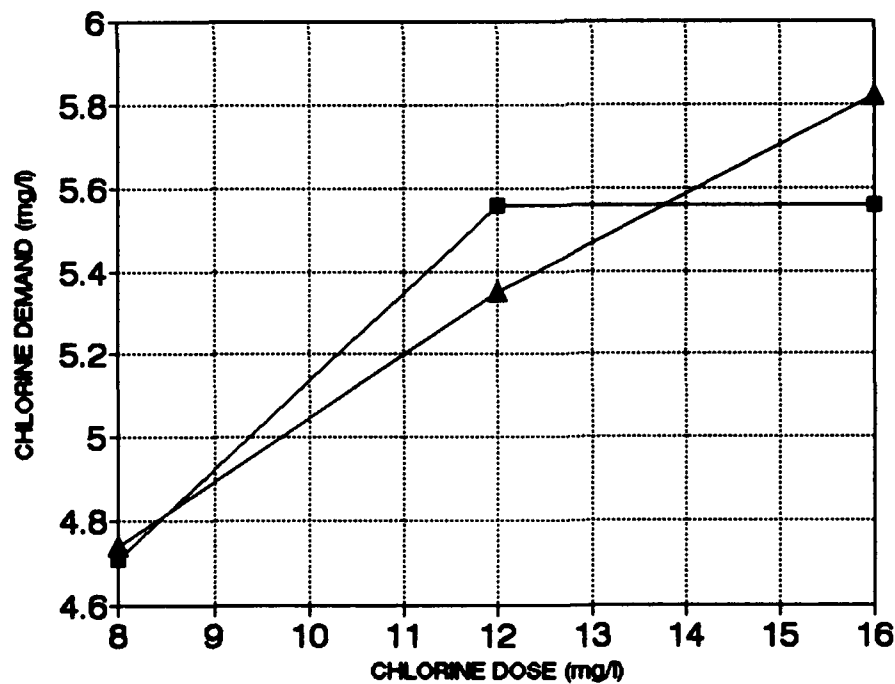**2HR CONTACT TIME KWRF FILTERED EFFLUENT**

Figure 3

TABLE 5

COMPARISON OF CHLORINE DEMAND AS MEASURED BY THE DPD METHOD FOR THIS RESEARCH VS RESEARCH CONDUCTED ONE YEAR AGO				
CHLORINE DEMAND (mg Cl2/L)				
DOSE (mg Cl2/L)	JUL 1991 1 HOUR CONTACT	JUL 1993 2 HOUR CONTACT	JUL 1991 24 HOUR CONTACT	JUL 1993 24 HOUR CONTACT
8.0	4.75	4.74	7.48	7.04
12.0	5.70	5.35	9.38	8.31
16.0	5.51	5.82	9.70	9.26

TABLE 6

SUMMARY OF CHLORINE DOSE VERSUS DEMAND FINDINGS FOR DPD TEST ON KANAPAHA WASTEWATER 24 HOUR CONTACT TIME			
DOSE (mg Cl2/l)	ABSORB	RESID CHLORINE (mg Cl2/l)	CHLORINE DEMAND (MG CL2/L)
8.0	0.256	0.96	7.04
	0.256	0.96	7.04
	0.256	0.96	7.04
	0.255	0.95	7.05
	MEAN	0.96	7.04
	STD DEV	0.005	0.005
12.0 DILUTION 4:1	0.246	3.68	8.32
	0.244	3.65	8.35
	0.251	3.75	8.25
	0.245	3.66	8.34
	MEAN	3.69	8.31
	STD DEV	0.047	0.047
16.0 DILUTION 4:1	0.454	6.80	9.20
	0.457	6.85	9.15
	0.447	6.70	9.30
	0.440	6.59	9.41
	MEAN	6.74	9.26
	STD DEV	0.114	0.114

CHLORINE DEMAND VS DOSE
KOTOB VS THIS STUDY

Figure 4
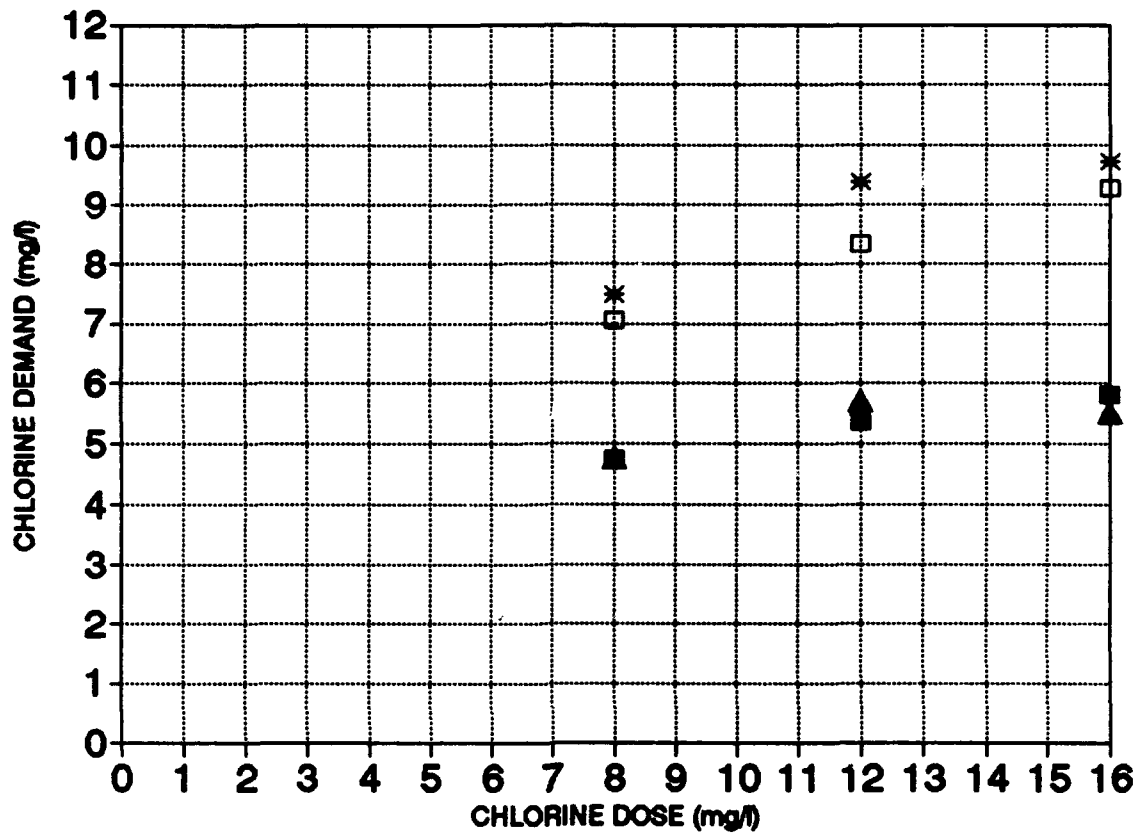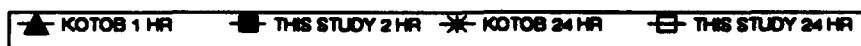
KOTOB 1 HR | THIS STUDY 2 HR | KOTOB 24 HR | THIS STUDY 24 HR

respectively. For both research studies, the observation that the rate of change of demand appeared to be highest between the 8mg/l dose and 12 mg/l dose was shown.

The 24 hour results are presented in Table 6 and Figure 6. Slopes from 8 mg/l dose to 12 mg/l dose were 0.48 and 0.32 for 92' and 93' results, respectively. For 12 mg/l to 16 mg/l, slopes were 0.08 and 0.24 for the 92' and 93' results, respectively. These are higher slopes than measured at 2 hours. This higher slope is a function of the dependency of reaction rates on concentration (chlorine residual). Additionally, these higher slopes may be attributed to the self-perpetuating nature of reactions whereby chlorine reacts with a chemical and activates it, thus enabling other chlorine atoms to react with other sites on the molecule.

The percent increase in chlorine demand as a percentage of residual at each dose also demonstrates the theory discussed above. From the 2 hour reaction time to the 24 hour reaction time, % increases in demand as a function of residual chlorine for results obtained in this research were 70.6%, 44.5%, and 33.8% for 8mg/l, 12 mg/l, and 16 mg/l doses, respectively. These corresponded to actual demand increases in mg/l chlorine of 2.33, 2.73, and 3.16 for the 8, 12, and 16 mg/l doses, respectively. Note that the percent decrease difference between 8 mg/l and 12 mg/l was substantially greater than from 12 mg/l to 16 mg/l.

If demand were not a function of dose the lines in Figure 4 would be horizontal, with a slope of zero. Stevens, et al., in their study of THM formation from humic substances exposed to chlorine, found that when THM formation was plotted as a function of humic acid concentration, at a specific time, the plots showed a rapid rate of

increase of THM concentration to a point on the humic acid (dose) axis, then a drop off to almost a constant concentration with increased dose[18]. This is the same phenomena observed in this experiment. Stevens attributed the changing rates of THM formation as related to the apparent exhaustion of reaction sites of organics.

There are a multitude of organic and organic nitrogen compounds present in wastewater effluent, each with reaction rates with FAC which may be quite complex, many involving equilibrium relationships and competition between intermediate reaction steps. Trihalomethanes are just one group of reaction products from interactions between organics and FAC. As a group, however, THM formation appears to offer some insight into the overall relationship observed between chlorine dose and chlorine demand. Trends observed by Stevens[18] and Kotob[9] showed THM concentrations increasing rapidly with reactant dose, then not increasing as quickly beyond some reactant dose. This was the overall relationship observed in this study between chlorine demand (which reflects the amount of chlorine reacted) and chlorine dose. It is reasonable to hypothesize that chlorine may react with many other organics in the same way. That is, depleting available reaction sites at accelerating rates relative to increasing concentration of chlorine, then slowing down as the reaction sites are exhausted and kinetics of the reaction are less influenced by FAC concentration than time.

These observations have implications for treatment and regulation. To minimize formation of chloro-organics and chlorinated organic-nitrogen compounds, chlorine dosing should be maintained as low as possible while still achieving disinfection needs. The contact time between high doses of chlorine and wastewater should be minimized

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while still achieving desired water quality. Precursors such as humic materials should be removed prior to chlorination to the extent feasible. THM concentrations should be closely monitored as they vary with chlorine dose applied. Although THMs are the only disinfection by-products currently regulated in drinking water, new federal rules will be proposed in 1993 which will include maximum contaminant limits for other chloro-organics.

Effect of Chloramines on FAC Residual Measurements

In order to examine the effects of chloramines on FAC residual measurements, a known concentration of ammonium chloride was added to a chlorine-demand-free DDI sample and dosed with known concentrations of chlorine. The object of this experiment was to examine how the analytical tools of amperometric titration and DPD analysis would perform in the presence of potentially interfering chloramines. Chlorine residual and chlorine demand test results for both of these methods are summarized in Table 7, while additional supporting data are presented in Tables 8 and 9.

Samples were dosed to produce chlorine/ammonium-N mass ratios of 4, 6, and 12, and measured for FAC two hours later. Breakpoint curve theory explains what happens to chlorine residual in the presence of ammonia as the applied chlorine dose is increased. Initially, monochloramine is created as the chlorine reacts with ammonia, as shown in the equation below[1].

$$Cl_2 + H_2O \rightarrow HOCL + H^+ + Cl^- \quad Kh = 4 \times 10^{-4} \text{ (4)}$$

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \text{ (5)}$$
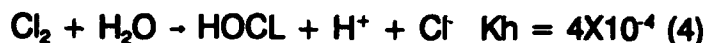
Highest reaction rates are observed between pH 7.5 and 9.3[15]. At pH ratios between 7

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TABLE 7

	DPD METHOD			AMPEROMETRIC METHOD		
FAC CHLORINE RESIDUALS MEASURED BY DPD METHOD VERSUS AMPEROMETRIC METHOD FOR VARYING CHLORINE TO AMMONIUM CHLORIDE-N RATIOS IN DDI 2 HR REACTION TIME						
	UNITS IN MG CL2/L					
CL2/N MASS RATIO	RESID MEAN	DEMAND MEAN	STD DEV	RESID MEAN	DEMAND MEAN	STD DEV
4.0	0.20	3.80	0.065	0.00	4.00	0.000
6.0	0.22	5.78	0.012	0.00	6.00	0.000
12.0	2.10	9.90	0.004	2.87	9.13	0.076

TABLE 8

CHLORIDE DEMAND AS A FUNCTION OF CHLORINE TO
AMMONIUM CHLORIDE-AS NITROGEN RATIOS
DPD METHOD 2 HOUR REACTION TIME

	DPD METHOD		
RATIO (MG CL2/MG NH4CL-N)	ABSORB	FREE RESIDUAL CHLORINE (MG CL2/L)	FREE CHLORINE DEMAND (MG CL2/L)
4.0	0.072	0.27	3.73
4.0	0.038	0.14	3.86
4.0	0.049	0.18	3.82
MEAN	0.053	0.20	3.80
STD DEV	0.017	0.065	0.065
6.0	0.058	0.21	5.79
6.0	0.057	0.21	5.79
6.0	0.063	0.23	5.77
MEAN	0.059	0.22	5.78
STD DEV	0.003	0.012	0.012
12.0	0.560	2.10	9.90
12.0	0.562	2.11	9.89
12.0	0.562	2.11	9.89
MEAN	0.561	2.10	9.90
STD DEV	0.001	0.004	0.004

TABLE 9

	CHLORINE DEMAND AS A FUNCTION OF CHLORINE TO AMMONIUM CHLORIDE AS NITROGEN RATIOS AMPEROMETRIC METHOD 2 HR REACTION TIME		
	AMPEROMETRIC METHOD		
RATIO CL/ NH4-N	VOL TITRATE AGENT	FREE Cl2 RESIDUAL (mg Cl2/L)	FREE CHLORINE DEMAND
4.0	0.00	0.00	4.00
4.0	0.00	0.00	4.00
4.0	0.00	0.00	4.00
	MEAN	0.00	4.00
	STD DEV	0.000	0.000
6.0	0.00	0.00	6.00
6.0	0.00	0.00	6.00
6.0	0.00	0.00	6.00
	MEAN	0.00	6.00
	STD DEV	0.000	0.00C
	DILUTION 5		
12.0	0.57	2.85	9.15
12.0	0.56	2.80	9.20
12.0	0.59	2.95	9.05
	MEAN	2.87	9.13
	STD DEV	0.076	0.076

and 8, 99% of the free chlorine in a solution with a chlorine to ammonia-N mass ratio of 5 is converted to NH_2Cl in 0.2 seconds[1]. This is about where the "hump" of the breakpoint curve is reached and chlorine residual is maximum.

At a Cl_2/N mass ratio of 4 and a reaction time of 2 hours at neutral pH, all FAC should have been substituted for hydrogen on ammonia molecules, and chlorine residual should be all monochloramine with no free chlorine remaining. Even so, the methods provided different results.

The DPD method measured a mean FAC residual of 0.20 mg Cl_2/l. The standard deviation was 0.06 for this method. The spectrophotometer digital readout for these samples fluctuated greatly and was very unsteady. The readout was observed to quickly drift upward with time while a sample was being analyzed. The amperometric method, on the other hand, measured no FAC.

At a mass ratio of chlorine/ammonium chloride-N of 6, breakpoint theory would dictate the monochloramine concentration should decrease as dichloramine was slowly produced, and it, in turn, decomposed to form nitrogen gas. The formation rate for dichloramine is considerably slower than that for NH_2Cl, and is favored at low pH (less than 5) (see eqn 6).

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \quad (6)$$

Above pH 7 nearly all chloramine from the hump to the breakpoint will be monochloramine, while below pH 7 some dichloramine will be formed[15]. Hence, for the near neutral pH in this experiment, there would be nearly all monochloramine, with some dichloramine in equilibrium with it. There should be no FAC.

The DPD results differed from prediction, showing a mean residual of 0.22 mg/l. Here, too, the spectrophotometer reading drifted upward, but more slowly than for the previous set of samples. Once again, the amperometric results showed no detectable FAC.

The logical conclusion is the DPD method was providing erroneous results at these chlorine-to-ammonia-N ratios. Work done by several other researchers supports this assertion. A good starting point is the Hach DPD Powder Reagent instruction sheet, which states "high concentrations of monochloramine will interfere with the results of the free chlorine test[19]." But what are high monochloramine concentrations?

Cooper, et al. studied the effects of monochoramine, dichloramine, and trichloramine on the analysis of FAC[13]. Since conditions in this experiment did not favor formation of NCl_3 (low pH and chlorine-to-ammonia-N molar ratio of at least 3), it will not be addressed.

At a monochloramine concentration of 3.5 mg/l as Cl_2/N in chlorine-demand-free water, an apparent NH_2Cl breakthrough of 4.6% percent per minute was measured. This would equate to 0.161 mg Cl_2/l. This research found an apparent residual which was very close to Cooper's (in this research, it took 1 minute after addition of reagent to take readings, and the Cl_2/N ratio was 4.0 not 3.5).

At an NH_2/Cl dose of 6.4 mg/l, Cooper found an apparent FAC reading of 0.2 mg/l which is just under the 0.22 measured in this research. Cooper's research also explains the upward migration on the spectrophotometer.

According to the same study, dichloramine interfered with the DPD test only at 20

mg/l (dichloramine as Cl_2, added to chlorine-demand-free water). Certainly, not even a very small fraction of this level was approached at any time during the experiment.

Guter tested the ability of test kits including the DPD-colorimetric procedure-on their ability to distinguish FAC from combined chlorine, specifically the monochloramine and dichloramine fraction. In his study, he found the DPD test gave false-positive readings on 14 of 16 tests done on effluent from wastewater treatment plants after secondary treatment (and lab dilution by a factor of 3)[8].

Cooper et al. tested laboratory solutions containing no FAC and various concentrations of monochloramine and dichloramine. Of twenty solutions, the amperometric titration of these solutions showed no FAC[13].

At a 12 mg/l Cl_2/NH_4Cl-N ratio, both methods measured a FAC residual which is consistent with breakpoint theory. The breakpoint theoretically occurs at about a mass ratio of chlorine-to-ammonia-nitrogen of 7.6:1. This ratio is based on equation 8 which shows nitrogen gas as the reduced product.

$$3 \ HOCl + 2 \ NH_3(aq) = 3 \ H^+ + 3 \ Cl^- + 3 \ H_2O + N_2(g) \quad (7)$$
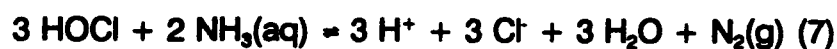
At the breakpoint, all the ammonia is theoretically oxidized and all the chlorine reduced to chloride[6]. The ammonia reaction with chlorine is typically over in 30 minutes with 75-80% loss of nitrogen[1].

The amperometric method measured a demand of 9.13 mg/l while the DPD method measured a demand of 9.90 mg/l FAC. In this experiment, unlike earlier ones, there appeared to be a negative bias on the DPD FAC residual measurement since it gave a lower free chlorine concentration than the amperometric method. Nothing in the

literature was found to support this observation. It is more likely error was introduced in dosing the amperometric reaction vessels.

The difference in precision among the four runs for each method as measured by standard deviation was very small: 0.076 for amperometric, and 0.004 for DPD method. These results both showed higher than theoretical demand by the ammonia for chlorine. These results are supported by the literature.

According to White, in wastewater treatment practice the breakpoint has been shown to occur when the ratio of chlorine to ammonia-N is closer to 10:1 by weight. This increase is caused by formation of nitrogen gas, nitrate, and nitrogen trichloride whose reactions with chlorine are stoichiometrically more demanding on the chlorine[1]. Formation of nitrate (from ammonia reactions with chlorine) occurs on a 4:1 molar basis as shown in equation 7.

$$4\ Cl_2 + NH_{3(aq)} + 3\ H_2O \rightleftharpoons 8\ Cl^- + NO_3^- + 9\ H^+ \quad (eqn\ 7)$$

This corresponds to a Cl_2/N mass ratio of 20.3. One possible ammonia reaction hypothesis to explain this experiment's findings would show 88% of the ammonia reacting with FAC to form nitrogen gas and 12% reacting with FAC to form nitrate. This explanation is reasonable and compare favorably with results found in the literature[1].

Summary and Conclusions

Summary

Three methods for measuring free available chlorine were considered for use in this study: DPD method, FACTS method, and amperometric method. These were chosen because of their accuracy and precision in measuring FAC based on a review of the literature. The FACTS method was abandoned for sample analysis after several efforts were unsuccessful in producing reliable results. The difficulty of dissolving the indicator (syringaldazine) in 2-propanol solution had been reported in the literature.

The DPD method and amperometric method were compared for accuracy and precison. Wastewater samples were collected from the KWRF on three separate days, dosed with 8 mg/l chlorine, and left to react for two hours. Four runs were made with both methods of each day's sample. There was no significant difference at the 95% confidence interval between the mean FAC results measured by the two methods on two of the three days. The DPD method was more precise and accurate than the amperometric method for this sample matrix. The mean standard deviation for the DPD method over the three days was 0.033, while for the amperometric method it was 0.148. The higher imprecision in the amperometric method was probably related to sample dosing. One dosed sample was used for the DPD method while amperometric samples were individually dosed to stagger analysis time.

The amperometric method consistently measured lower FAC residuals than did the DPD method. This was attributed to losses due to volatility of chlorine. In a 1 mg/l

chlorine in DDI sample, the mean chlorine recovery in seven runs after 24 hours reaction time was 99% for the DPD method and 94% for the amperometric method.

KWRF samples were dosed at 8, 12, and 16 mg/l and left to react for two hours to determine the effect of chlorine dose on chlorine demand. The DPD and amperometric methods were used to determine FAC residuals. Chlorine demand was found to increase with chlorine dose. The amperometric method and DPD method both indicated an increase in demand with dose up to the 12 mg/l chlorine dose.

When this study's demand versus dose results obtained by the DPD method were compared to findings made by Kotob two years ago, consistent trends were observed. Chlorine demand appeared to increased with dose up to about 12 mg/l, then the rate of change of demand with dose decreased. This observation is explained by the dependency of the reaction rates between organic materials (such as humics) and organic nitrogen compounds (such as amines and amides) on reactant concentration (in this case the reactant being FAC). The decrease in slope can be attributed to exhausion of reaction sites.

At each dose, an increase in chlorine demand was observed between the two hour and 24 hour reaction times. This is related to the time-dependency of the chlorine reactions with organics and organic nitrogens. For many of the organic compounds, time may more strongly dictate the extent of reaction than chlorine concentration due to reaction kinetics.

The effect of chloramines on FAC residual measurements was determined by dosing 1 mg/l ammonia-N in DDI solutions with chlorine to produce 4, 6 and 12 Cl_2/N

mass ratio samples. Four runs were made with each method for the sample solutions. Significant monochloramine intrusion was observed in DPD analyses at Cl_2/N mass ratios of 4 and 6. Apparent FAC residuals of 0.20 and 0.22 were measured with the DPD method. The amperometric method measured no FAC in these solutions. This was the theoretical response since the breakpoint had not been achieved. In the 12 mg Cl_2/N solution, FAC residuals of 2.10 and 2.87 were measured with the DPD method and amperometric method, respectively. The higher residual measured with the amperometric method was probably the consequence of error introduced in dosing rather than a negative interference on the DPD FAC measurement. The breakpoint was found at 9.90 and 9.13 Cl_2/N for the DPD and amperometric method, respectively. These values are larger than the theoretical breakpoint of 7.6 mg Cl_2/N. Measured values were consistent with those reported in the literature.

Experiments in this study using KWRF wastewater samples would not be expected to have chloramine intrusion in the FAC residual measurements made with the DPD method. Because the KWRF denitrifies their wastewater, very low concentrations of ammonia would be expected. The chlorine dose applied in this study easily exceeded the breakpoint for the denitrified KWRF wastewater samples.

Conclusions

The DPD and amperometric methods are both excellent tools for measuring FAC. Both techniques have limitations and strengths which should be considered prior to running FAC tests.

The amperometric method will certainly remain a top laboratory option for performing FAC tests. The procedure is extremely specific for FAC and results are not positively biased by likely interferences, especially from monochloramines. This procedure can also accurately and precisely measure concentrations of monochloramines and dichloramines. Hence, for research work on disinfection, such as the use of chloramines as disinfectants, and detailed routine analyses at wastewater treatment facilities where chloramine concentrations are needed for treatment schemes, this is the procedure of choice. The amperometric technique, even if not used as the primary routine measurement technique, should certainly be used, where available, as a check on the accuracy of other methods.

For routine analyses where convenience, rapidity, and ease of analysis are primary considerations, and where FAC is the only information needed, the DPD method used in this report is not appropriate for waters with appreciable ammonia concentrations. The DPD method is not specific for FAC. This technique is, however, an extremely accurate and precise method for waters without appreciable ammonia content.

The DPD procedure can be and should be modified if it is to be used for FAC measurement. The DPD-Steadifac procedure uses thioacetamide to eliminate positive interference from monochloramine and dichloramine in the free chlorine measurement[3]. This modified procedure, not used in this research, is reportedly very simple, quick, precise, and accurate. The Steadifac-procedure has comparable accuracy and precision to the DPD-colorimetric procedure when they are both used in chloramine-free environments[9].

The DPD-Steadifac procedure should be a serious candidate for method of choice for pool water testing and testing of wastewater samples.

There are treatment implications related to the finding that chlorine demand increases with chlorine dose and reaction time. Chlorine dosing should be minimized while still achieving desired disinfection. Chlorine dosing at the KWRF should be maintained at the lowest levels which achieve disinfection requirements. Annually, when the United States as a whole is considered, several thousand tons of chloro-organics are released into aquatic systems as a consequence of chlorination[17]. The net effect of this may be more significant than we presently know. Since excessive chlorine dosing results in greater chlorine demand, it is sensible to seek means to minimize it. One way to do this is to use reliable and accurate FAC residual tests to ensure that appropriate disinfection potential remains in chlorinated water.

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APPENDIX

APPENDIX 1

USE OF THE AMPEROMETRIC TITRATOR

This description is provided so that future users of the amperometric titration unit can avoid the difficulties typically encountered by novice users of this method for measuring free chlorine residual.

First, check the platinum electrode and ensure it is free of spots or any other signs of contamination. The electrode is extremely sensitive and slight problems with its platinum surface may lead to errors in measurement. The electrode surface should be cleaned with a culture swab dipped in a non-abrasive soap solution. Rub the electrode surface lightly. Check its cleanliness by dipping the electrode in water, then holding the electrode horizontally to see whether water forms a smooth flat covering on the electrode surface or forms individual drops. The latter indicates the electrode is not clean. Repeat this for both sides of the electrode.

The electrode must now be sensitized. This means it needs to become accustomed to measuring reducible species in a sample. Sensitize the electrode with chlorine solutions in DDI at low concentrations (0.5 mg Cl_2/l or lower). It may take several efforts to steady the needle reading on the microammeter panel. Continue running samples through until you are confident the instrument will provide consistent readings and behavior.

When running samples with this method, refill the titrant bottle with titrant each day. Dispense and refill the titrant delivery system until all air bubbles are out of the hosing

and delivery pipet. Air bubbles can create significant errors in this method as they will sometimes coagulate then move together accounting for as much as an apparent use of 0.1 ml of titrant.

Before running your sample, DDI rinse the electrode and pipet. Then refill the graduated 2 ml pipet with titrating solution. When this is done, deliver one or two drops through the delivery tip. Do not leave a partial drop hanging from the delivery tip as this can lead to error. Carefully remove the previous sample and without damaging the pipet tip, put the new beaker in place and lower the assembly containing the pipet and electrode into the next sample.

When running the titration, you should start on the low sensitivity setting unless you believe the sample to contain less than 0.3 ppm chlorine. Then slowly titrate adding about 0.10 to 0.20 ml of titrant until you notice a marked decrease in the meter's downward response. At this point, you are in the vicinity of the endpoint and you should switch to high sensitivity.

While on high sensitivity slowly add titrant and observe meter's response. Occasionally the needle will bounce up a small amount, then drop below the original indication. You are interested in the needle's final resting point. Another potential (and likely) problem the novice titration unit user may have is distinguishing between a very slight downward drift in the meter indication (caused by volatility of chlorine) and the needle movement caused by titrant reaction with chlorine. When the titrant reacts with chlorine, the indicator responds deliberately and somewhat briskly. As you near the endpoint, use the suppression control knob to keep the microammeter reading between 15 and 20 microammeters. Otherwise, you may not be able to distinguish betweeen

unwanted electrolyte current (noise) relative to the sensitivity level at which the instrument is operating.

When the last small increment of titrant barely causes a downward change in current reading, record the result. You may need to repeat this several times until the next small increment causes no change in current reading and you are at the endpoint. You should add at least 0.05 ml to 0.10 ml slowly to be sure the meter reading does not drop after you think you have reached the endpoint. In fact, if you have indeed located the endpoint, the current reading should go up upon additional titrating agent delivery.

A typical amperometric titration on an unknown sample should take about 10 minutes, depending on whether you have properly sensitized the electrode, your experience level, and whether your sample contains more than 2 mg Cl_2/l or not. If so, you should dilute the sample and run it again since the additional time taken to titrate the undiluted sample may cause unacceptable chlorine loss through evaporation.

APPENDIX 2

FACTS METHOD

Standard Methods calls for using either chlorine-demand free 2-propanol or redistilled 2-propanol. The chlorine-demand free 2-propanol is made by dosing a volume of 2-propanol with chlorine, leaving the solution overnight with a free residual, then dechlorinating it by leaving the 2-propanol in sunlight.

Initially, an HPLC grade Fisher-Scientific 2-propanol was used directly (without either of the pretreatments described above). At a DDI/chlorine concentration of 2 mg/l, the FACTS test provided absorbances ranging from 0.950 to 1.155 on the Perkin-Elmer spectrophotometer set a 530 nm. Significant drifting was observed in the digital readout. At this time, Standard Methods was reviewed and it was noted a path length of 1 mm was required for high FAC residual measurements. Since the instrument uses sample cells with a 1 cm pathlength, it was decided to keep measurements between 0.1 and 1.0 mg/l which seemed to conform to the path length specifications in Standard Methods. Further readings at lower concentrations were random also. For instance, at a chlorine concentration of 0.5 mg/l in DDI, an absorbance of 0.5 was measured, while at 1.0 mg/l a range of 0.048-0.321 was observed. At this point the indicator solution itself become suspect.

Upon closer inspection, it was evident not all the syringaldazine had dissolved in the 2-propanol, so 30 minutes of ultrasonic agitation and another 60 minutes of gentle heating were employed to assist in the dissolution process. The dissolution problem was

noted by Gordon, et al as "the serious drawback of the FACTS test procedure is the insolubility of the syringaldazine in either 2-propanol or water[4]." The following day (after cooling), the mixture was filtered twice through a 0.45 micrometer filter pretreated to remove surfactants. Further absorbance readings were also unreliable. Several pH measurements were then made in an attempt to determine whether the buffer might be the problem. The pH of the buffer was 6.68 which is what Standard Methods called for. The buffer was found to maintain this pH when 1 mg/l chlorine was added to the DDI/buffer mixture. When syringaldazine was added, the pH went up to 7.22. A new solution of buffer was made and results were practically identical.

Dr. William J. Cooper[20] was consulted with by phone at this juncture. He advised the 2-propanol interfered with pH measurements and to rely on the buffer if its pH and make-up conformed to requirements. Additionally, he mentioned the 2-propanol has some chlorine demand which interferes with measurements. From his own work, he found unreliable outcomes using the syringaldazine/2-propanol reagent unless the isopropyl alcohol was re-distilled first. He said the identity of whatever interferes in measurements for FAC remains a mystery.

After the phone conversation, it was decided to order a better grade 2-propanol from Fisher (Optima Grade). Fisher Scientific technical representatives had no knowledge of the FACTS method or any previous feedback or research on chlorine demand associated with their Optima product. In the meantime, the Spec 21 was used to repeat past efforts to develop a standard curve for the FACTS method. Again, results were inconsistent.

When the Optima Grade isopropyl alcohol arrived, a new syringaldazine solution

was made up and a few FACTS test runs were performed. Results were similar to those obtained previously. The 2-propanol was then dosed with chlorine and found to have a significant chlorine demand. Two experiments were conducted to test for chlorine demand over 24 hours. The first, which was repeated again for confirmation, showed a chlorine demand of greater than 40 mg/l. The second showed this demand to be over 100 mg/l chlorine. A Chemistry Department professor was informally consulted with. He postulated that the chlorine was reacting with the propanol to form acetone, hydrochloric acid and water.

A final effort involved using DDI as the solvent for syringaldazine. Scant information on the solubility of syringaldazine was found, so this seemed a worthwhile option. Unfortunately, too little syringaldazine dissolved in the DDI, despite vigorous stirring, heating, and agitation. Results were barely above the blank level for even 1 mg/l chlorine dosed DDI. This is not a surprise. Bauer found the maximum color intensity to occur at a molar ratio of chlorine and syringaldazine of one-to-one. The drop-off in absorbance was dramatic below this ratio[5].

Clearly, if this method is to be pursued, one of the only alternatives remaining is to redistill 2-propanol as outlined in Standard Methods. It might be interesting to isolate the fraction of 2-propanol after distillation not to be used as solvent and analyze it with a mass spectrometer to determine what the interference might be. Another consideration is the way in which Bauer, the chemist who developed this FACTS procedure, carried out his work.

Bauer used a 0.1-1.0 ppm range for this technique, an area in which he found most reliable results and best linearity between absorbance and FAC concentration. He

prepared a stock syringaldazine in reagent alcohol solution of 0.1 % by dissolving 100 mg of syringaldazine in 100 ml of reagent alcohol with heat to aide in dissolution. It would seem from the previous discussion this would exacerbate the dissolution problem previously discussed ten-fold. Bauer used a reagent alcohol mixture of 90% ethanol, 5% methanol, and 5% isopropyl alcohol rather than pure isopropyl alcohol. Whether and how this would assist in dissolution over using pure isopropyl alcohol was not explored by this researcher nor was any literature found to support the assertion better dissolution would occr. In any case, Bauer made a fresh working solution daily from this stock by placing 8 ml of the stock in a 100 ml vol flask containing 15-20 ml reagent alcohol. He then added 50 ml of phosphate buffer (0.05 molar), and brought the total volume to 100 ml with reagent alcohol. With this working solution, he tested 10 ml samples with chlorine concentrations of 0.1-1 ppm with 1 ml of the working solution. Bauer noted that his buffered solutions when left standing at room temperature for 24 hours or more, showed a gradual decrease in color production[5]. Cooper's work, on the other hand, found the shelf life of the syringaldazine in 2-propanol solution to be at least a year[13].

Based on the literature, this method has great potential for FAC measurements and further work would probably support this. It is interesting to note, however, that according to a March 1978 questionnaire developed by the AWWA Disinfection Committee, regarding current practices by water utilities on chlorination of potable water, that of 332 respondents, 235 were using DPD, 165 amperometric titrator, 127 acid ortho-tolidine, 11 neutral O-T, 1 FACTS and 1 starch-iodide. The water which was disinfected came from a variety of sources. Some of the sources contained high ammonia-N concentrations[1].